Journal of Organometallic Chemistry, 52 (1973) C7–C10
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Homologation of β-silyl-α,β-unsaturated esters

ROBERT F. CUNICO, HONG MEE LEE and JAMES HERBACH
Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115 (U.S.A.)

(Received February 20th, 1973)

SUMMARY

Treatment of β-trimethylsilyl-α,β-unsaturated esters with diazomethane results in a stereospecific homologation to the corresponding γ-trimethylsilyl-α,β-unsaturated esters.

We wish to report that the reaction of diazomethane with β-trimethylsilyl-α,β-unsaturated esters results in the facile homologation of these species by formal introduction of a methylene unit between the silyl and alkenyl groups. Thus, both *cis*-(Ia) and *trans*-methyl 3-trimethylsilylpropenoate (Ib) are converted stereospecifically to the respective *cis*-(IIa) and *trans*-methyl 4-trimethylsilyl-2-butenoates (IIb).

$$\underset{\text{(Ia,b)}}{Me_3SiCH{=}CHCO_2CH_3} + CH_2N_2 \rightarrow \underset{\text{(IIa,b)}}{Me_3SiCH_2CH{=}CHCO_2CH_3}$$

When 0.5 g (3.2 mmole) of (Ia)[*] was treated with 15 ml (3.5 mmole) of a 0.23*N* ethereal solution of diazomethane, GLC analysis (bromobenzene internal standard) after 20 h at 25° indicated an 83% yield of (IIa), produced to the exclusion of (IIb). Identical treatment of (Ib)[**] led to a 75% yield of (IIb), again produced free of its stereoisomer (IIa).

In another run, the reaction of 1.4 g (8.9 mmole) (Ib) with 13.8 mmole diazomethane was monitored by GLC. The following percentage of (Ib) was converted after the time span indicated (minutes): 15 (1), 80 (13), 90 (26), 95 (30). Distillation then af-

---

[*] Obtained in 13% yield (b.p. 80–84°/80 mm) by hydroboration of methyl 3-trimethylsilylpropynoate (III) according to the method of Zweifel[1]. The reaction of diazomethane with 3-trimethylsilylpropynoic acid[2] afforded (III) (b.p. 71–75°/14 mm) without complication.

[**] Obtained in low yield (b.p. 75–77°/20 mm) from the reaction of 2-trimethylsilylvinyl magnesium bromide[3] with methyl chloroformate.

TABLE 1

CHARACTERIZATION DATA FOR SILYLESTERS

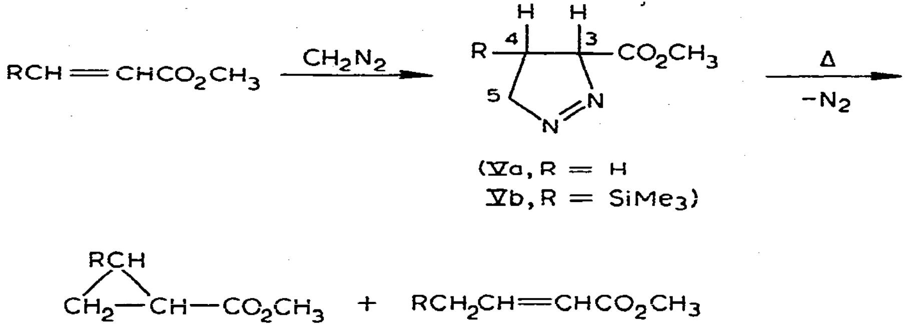
	Compound	NMR Spectrum [a]	Brutto formula	Analysis found (calcd.) (%)	
				C	H
(Ia)	$\overset{A}{Me_3}Si\overset{B}{CH}{=}\overset{C}{CH}CO_2\overset{D}{CH_3}$	δ_A 0.15s; $\delta_{B,C}$ 6.40s [b] δ_D 3.66s	$C_7H_{14}O_2Si$	53.24 (53.13)	8.75 (8.92)
(Ib)	$\overset{A}{Me_3}Si\overset{B}{CH}{=}\overset{C}{CH}CO_2\overset{D}{CH_3}$	δ_A −0.10s; δ_B 6.96 and δ_C 5.92 [c] (J_{BC} 19Hz); δ_D 3.45s		53.03	9.05
(IIa)	$\overset{A}{Me_3}Si\overset{B}{CH_2}\overset{C}{CH}{=}\overset{D}{CH}CO_2\overset{E}{CH_3}$	δ_A −0.18s; δ_B 2.22d (J_{BC} 9.5Hz); δ_C 6.28 and 6.10 (pair of t, J_{CD} 12Hz, J_{CB} 9.5Hz); δ_D 5.48d; δ_E 3.62	$C_8H_{16}O_2Si$	55.82 (55.77)	9.26 (9.13)
(IIb)	$\overset{A}{Me_3}Si\overset{B}{CH_2}\overset{C}{CH}{=}\overset{D}{CH}CO_2\overset{E}{CH_3}$	[d]		55.77	9.24
(III)	$\overset{A}{Me_3}SiC{\equiv}CCO_2\overset{B}{CH_3}$	δ_A 0.20s; δ_B 3.69s	$C_7H_{12}O_2Si$	54.14 (53.84)	7.82 (7.69)
(IV)	$\overset{A}{Me_3}SiC(CO_2\overset{B}{CH_3}){=}\overset{C,D}{CH_2}$	δ_A 0.12s; δ_B 3.66s; $\delta_{C\ or\ D}$ 5.97d; $\delta_{C\ or\ D}$ 6.67d (J_{CD} 3Hz) [e]	$C_7H_{14}O_2Si$	53.28	8.51

[a] Spectra obtained on CCl_4 solutions with $HCCl_3$ internal standard; chemical shifts reported to midpoint of multiplets; integration values were consistent with assignments. [b] Converged chemical shifts for vinyl protons. [c] AB pattern. [d] Spectrum essentially identical with that reported[4]. [e] Acetone internal standard.

forded 0.78 g (55%) of (IIb), b.p. 80–84°/18 mm (lit.[4], b.p. 80–89°/25 mm).

Location of the trimethylsilyl group on the vinyl position β to the carboxymethoxy function was found to be critical to the homologation process. Thus, attempted reaction between diazomethane and methyl 2-trimethylsilylpropenoate (IV)[*] resulted in the slow disappearance of (IV) over several days, but no homologation product (or any other material of similar volatility) could be detected by GLC.

These observations seem best interpreted in terms of the known chemistry of pyrazoline intermediates formed by 1,3-cycloaddition of diazo species to α,β-unsaturated esters[5]. Pyrazolines such as (V), for example, undergo thermolysis to yield varying proportions of cyclopropane and homologous olefinic product:



(Va, R = H
Vb, R = SiMe$_3$)

The latter transformation has been described[5] as entailing the migration of a C-4 hydrogen[**] in (Va) to C-5 concerted with elimination of nitrogen, resulting in an overall stereospecific[***] homologation of the original α,β-unsaturated compound. Although in the present case, we have as yet no direct evidence for the intermediacy of (Vb), facile migration of the trimethylsilyl group to C-5 within this species, concerted with loss of nitrogen, would offer an explanation for the direction and stereospecificity of the reaction. That the trimethylsilyl group migrates to the apparent exclusion of C-4 hydrogen may be a function of conformational preferences which orient this group in a position most favorable for migration, or may be due to an inherent enhanced ability for migration of the silyl group over hydrogen.

The details, scope and synthetic utility of this transformation are presently under investigation.

Characterization data for compounds I—IV are given in Table 1.

---

[*] Prepared (b.p. 53–56°/18 mm) from the acid-catalyzed esterification of 2-trimethylsilylpropenoic acid[3].

[**] Alkyl and aryl migrations have also been observed in the thermolysis of pyrazolines in which a cyano function has replaced hydrogen at C-3 [6].

[***] The original cycloaddition is known to be stereospecifically *cis*[7].

REFERENCES

1 J. Plamondon, J.T. Snow and G. Zweifel, *Organometal. Chem. Synth.*, 1 (1971) 249.
2 G.E. Bennett and W.W. Lee, *U.S. Patent No. 2,887,371; Chem. Abstr.*, 53 (1959) 19883f.
3 V.F. Mironov, A.D. Petrov and N.G. Maksimova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1959) 1864.
4 W.P. Weber and R.A. Felix, *Tetrahedron Lett.*, (1971) 1445.
5 D.E. McGreer and I.M.E. Masters, *Can. J. Chem.*, 47 (1969) 3975 and previous papers in the series.
6 D.E. McGreer and Y.Y. Wigfield, *Can. J. Chem.*, 47 (1969) 3965 and references therein.
7 R. Huisgen, *Angew. Chem. Intern. Ed. Eng.*, 2 (1963) 633.